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EXPERIMENTAL INVESTIGATION ON THE DETERMINATION OF THE SURFACE TENSION OF LIQUIDS BY THE MAXIMUM PRESSURE FOR THE FORMATION OF BUBBLES

B. Ya. Teytel'baum,

Lab of Phys and Colloid Chem

of Rostov State U imeni V. M. Molotov

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The method of measuring surface tension at the liquid-gas boundary by the maximum pressure for the formation of bubbles is based on the well-known fact that when gas (air) passes slowly through the liquid under investigation in the form of separate bubbles, the pressure of the gas is determined by the amount of surface tension of the liquid [1, 2]. (As a curiosity, let us point out that in the Russian edition of Fizicheskaya Khimiya by Getman and Daniel's (Vol XII, 1941), the editor of the translation states in a note that the P. A. Rebinder's method was based "on a comparison of the rates of bubbling the air through the fluid being tested and a standard fluid").

In Rebinder's apparatus [3], based on this method, air instead of being forced through the capillary opening, was sucked out of the space over the liquid. The tip of the capillary came in contact only with its surface. The surface tension is calculated from the relation:

$$\sigma = A \cdot p_{max}$$

The value of A (the "tip constant") is determined from measurements of p_{max} for a standard fluid; p_{max} is most conveniently measured in the column heights of a fluid poured into a manometer, for example in centimeters of a toluene column. The tips used in the work have openings of the order of 0.1-0.05 mm which widen upwards immediately beyond the capillary opening.

To obtain a reliable value for σ, a slow passage of air is required, especially in the case of viscous solutions. Great velocities are feasible not only because of the incomplete attainment of the adsorption equilibrium in the solutions, but also because groups of two to three bubbles rather than single ones were formed, and it was difficult to make an accurate record with a manometer.

Certain improvements in the method were made by Trifonov [4]. Figure 1 shows the diagram of Rebinder's apparatus as used in Trifonov's laboratories. Here K is a narrow "buffer" capillary; MK is a micro-cock; M, the toluene manometer; P, Rebinder's test tube; O, a calcium chloride tube used to dry the air; G, a "gooseneck" introduced to eliminate the possibility of fractionating the vapor of the solutions into the test tubes while the air is passing through them. In the gooseneck the air passes over the surface of the solution and becomes saturated with its vapors.

Our problem was to explain in what manner different constructional features of the apparatus and experimental conditions affected the value obtained for σ.

Let us examine in detail the mechanism of bubble formation during changes by the Rebinder method. For the sake of simplicity, instead of a capillary of the above-mentioned type, we will use a capillary with a radius equal to the radius of the tip. As the vacuum in the test tube is increased the meniscus level in the capillary will drop until the meniscus hemisphere extends out into the liquid and a bubble is formed. When the vacuum is further increased, the bubble becomes unstable and may break away under favorable conditions, for instance, if the capillary is bent in the form shown in Figure 2, so that the shape of the tube does not obstruct (sterically) the emergence of the bubble. However, since this obstruction is present in ordinary tips, the bubble does not break away but grows until the surface of the cut end of the capillary cannot retain it (Figure 2b). Once the excessive pressure in the capillary has reached its maximum, the growth of the bubble requires no further evacuation of the air in the system and therefore proceeds very rapidly. The floating bubble bursts and increases the pressure in the system. Thus, until maximum pressure is obtained, there is no current of air through the whole system; it is, in effect, sealed by the liquid in the capillary. As soon as the pressure reaches its maximum, a certain amount of air is sucked through O and G.

Since the pressure in the capillary tip is equal to one atmosphere and the maximum pressure is determined only by the amount of the vacuum created in the test tube, the pressure depends not on the resistance exerted against the air by the buffer capillary, micro-cock, drier and gooseneck but solely upon the tip constant and the surface tension of the liquid. (To measure σ for liquids which act chemically on rubber and cork stoppers Trifonov suggested using a test tube with a mercury stopper. Since such a test tube is equivalent to Rebinder's ordinary test tube with a mercury manometer attached in parallel to it (and to the manometer M), the use of a mercury seal, regardless of the quantity of the mercury in it, can not affect the measured amount of maximum pressure for forming bubbles. An experimental check confirmed our statement).

The amount of air passing through the device in 1 second (the force of the air current) depends on the rate at which the vacuum is created, and it becomes smaller as the resistance to the air exerted by parts of the apparatus-R_K, R_{MK}, R_O, R_G, and R_p grows larger. Here R_p is the resistance to the air passing through the fluid in the Rebinder test tube itself and may be assumed to be approximately zero. The non-dependence of the force of the air current on the properties (chiefly, viscosity) of the liquid may be the criterion for the equality $R_p = 0$.

When passing through the capillary tip, the air has a greater dynamic pressure in the narrow part than in the wide part of the tube. The pressure difference increases as the tube becomes significantly narrower, the narrow part longer, and the air current more rapid. Consequently, at the moment of bubble growth the pressure at the tip of the capillary is greater than the atmospheric pressure. At high velocities, it may, in spite of a certain decrease of vacuum in the test tube after the escape of the bubble, form a second bubble, and sometime even several, after the first one. (Note: Besides, the passage of bubbles is stimulated by a sucking action caused by the abrupt lowering of the level in the manometer after the maximum pressure has been reached). Hence, using long pieces of capillary as capillary tips is not possible. On the contrary, a tip shape where the narrow part of the capillary immediately widens out assures the passage of separate bubbles, since the total pressure (atmospheric + dynamic) differs little from one atmosphere. A similar observation was made by Schuetz in his experiments in producing foam [5].

The minimum radius r corresponding to the maximum pressure p_{max} is determined, as we know, from the relation $r \cdot p_{max} = 2\sigma$. Actually, however, the radius of the bubbles which have broken away has nothing in common with this quantity and is determined by the mechanical, or more accurately the steric conditions of their formation.

It is possible to estimate the dimensions of a bubble from the change in the pressure on the system. At the moment of bubble formation the pressure in the test tube equals $1-p_{max}$. After the escape of one bubble of v volume the pressure is increased to 1-p. If we assume that the volume of the system (from the microcock to the capillary tip) is constant and equal to V, we shall have $(1-p_{max}) \cdot V + 1 \cdot v = (1-p) \cdot V$. Hence, specifying that $p_{max} - p = \Delta p$, we shall find that $v = V \cdot \Delta p$. Expressing atmospheres in centimeters of the toluene column, we shall obtain:

$$v = \frac{V}{K} \Delta h,$$

where for a temperature of 25°K equals 1187, or approximately 1200.

The force of the air current may be calculated by the volume of the bubbles and the number of them liberated in a unit of time (for instance, 1 minute).

Working Method

To verify experimentally all the considerations stated above, a method for objective recording of the pressure was required. This would permit operation at different velocities of the air flow and a graphic comparison of the pressure under varied experimental conditions. For this purpose we constructed a photographic manograph.

The manograph works on the following principle: An image of the meniscus of the fluid in the manometer is projected by a beam of parallel rays from a projection lamp through a narrow aperture onto photographic paper moving past the aperture. The paper (4.5 x 12) in a special paper holder is fed by a small Warren motor ensuring linear velocities of the order of 12 cm per minute (in some experiments the velocity was considerably greater, reaching 6 cm per second). There is a knot in the thread connecting the motor and the holder. The manometer is capable of vertical movement, so that at any pressure the meniscus can be placed against the aperture. In our experiments we used both the ordinary U-shaped manometer (in which case we photographed only one upper surface) and an L-shaped manometer with one of the elbows greatly widened. In the latter case we photographed the elbow part but calculated the drop in the level in the wide elbow during the rise of the fluid in the narrow one. Before the exposure was begun, the surface levels were set at zero. The millimeter graduations were projected at the same time as the manometer image.

A centimeter scale, illuminated (when the) aperture is opened, can be projected separately. Figure 3 gives the diagram of the electrical system of the apparatus.

The apparatus in making determinations operates as follows:

1. By pressing a button twin switches V of the motor and S of the solenoid are closed; then the projection lamp L is turned on, the core Y is drawn into the solenoid, opening the scale aperture, and the contact switch Z_1 is opened so that the motor remains disconnected; this condition is maintained while the button is pressed; now the centimeter dial is photographed.

2. The button is released, the solenoid switch K is opened, and the motor switch remains closed; the projector lamp remains lighted, the core Y returns to its original position, closing Z_1 and switching on the motor at the same time; the scale aperture is closed; the driving thread is reeled up on the motor pulley, drawing the holder past the aperture, and a manogram record is produced.

3. The knot on the driving thread reaches the contact switch Z_2 and opens it; the motor is stopped, the projection lamp is disconnected; the exposure is finished.

4. When the button is pressed the system returns to its original position.

Figure 4 shows one of the prints we obtained. The prints are "read" by a multiple readin, for each of the "reliable" maxima of the manogram when observed through a 5-10 X lens.

Data From the Experiments

Individual "Waves". Records of individual "waves" (on quickly moving paper) facilitate explaining the type of the pressure change during the formation of a bubble (Figure 5). After the maximum pressure has been reached at A, it is observed to drop, and this is followed by periodic damping pressure variations caused by mechanical oscillations of the level in the manometer; after this the pressure along CD grows until it again reaches the maximum. The closeness of CD to a straight line makes it possible to determine the drop in pressure Δh for the escape of one bubble, as shown in Figure 5.

The fall in pressure--or, in other words, the lowering of the manometer level--was, as we saw, proportional to the volume of the bubble. In the passage of double bubbles Δh is invariably exactly twice as large as in the case of ordinary bubbles.

It is very characteristic that the value of Δh (and, consequently, the volume of the escaping bubble) does not depend on the surface tension of the fluid. Thus, at room temperature, Δh proves to be identical for pure water and for one percent solutions of glyerine, and of methyl, ethyl and isoamyl alcohols.

Effect of Viscosity. Viscosity, on the contrary, has a considerable effect on the size of Δh (but not on p_{max}). The greater the viscosity, the greater is the obstacle created to the breaking away of the bubble and the greater is its size at the moment of breaking away.

We took a series of ma ograms with glycerine at different temperatures, while the other experimental conditions remained the same. Table 1 gives the calculations made from these monograms. (Note: In all calculations the volume of the system V was taken to be approximately equal to 25 milliliters). As will be noted, the dimensions of the bubble decreased with the temperature (with the viscosity).

It is noteworthy that the product of the volume of the bubbles times the number of bubbles given off in a unit of time (the velocity of the passage of air) remains practically constant at all temperatures. This proves that the fluid in the test tube is not of itself a resistance to the passage of the air, thus confirming our opinion that $R_p = 0$.

Table I

Yield of Air Bubbles

Temperature in °C	0	25	55	80
Number of bubbles in 1 min. n	2.82	4.72	11.45	14.56
Δh/2 (cm)*	3.75	2.15	0.89	0.70
Volume of bubble v in ml	0.156	0.0898	0.0372	0.0292
Diameter of bubble in cm	0.67	0.56	0.42	0.38
Velocity n · v (ml/min)	0.438	0.424	0.424	0.425

*Drop of the level in one of the elbows of the U-shaped manometer.

In our opinion, the change in the value of Δh can serve as an approximate method for determining of the viscosity of fluids. A theory of the method has yet to be developed, but its utility for technological purposes is obvious.

The Effect of Air Resistances. We verified the non-dependence of the value of maximum pressure on the connection between the drier and "gooseneck" in the following manner. A manogram was taken while the capillary tip was in contact with the atmosphere through a three-way cock, and after several "waves" the system composed of the "gooseneck" and the calcium chloride tube was switched in by a turn of the cock (several forms of different sized tubes--straight and U-shaped--were tested packed to different densities). The height of the maxima was completely identical in all cases.

Table 2

Effect of the Resistance of Various Parts of the Apparatus on the Bubbles Size and Separation Rate.

No. of Experiment	1	2	3	4	5
$\Delta h_1/2$	10.7	10.7	10.4	11.0	11.6
$\Delta h_2/2$	9.0	8.0	9.3	7.0	8.0
n_1	8.4	9.4	9.7	11.4	7.46
n_2	9.1	12.3	12.3	17.8	11.4
V_1	0.0448	0.0448	0.0434	0.0458	0.0484
V_2	0.0376	0.0334	0.0388	0.0292	0.0334
$n_1 V_1$	0.389	0.422	0.420	0.526	0.360
$n_2 V_2$	0.342	0.412	0.476	0.520	0.380

When the gooseneck and drier were switched in, Δh decreased (the size of the bubbles decreased), but the rate of formation of bubbles increased. Hence, the amount of air passing in a unit time ($n \cdot V$) depends very little on the resistance exerted against the air by the drier and gooseneck. This is confirmed by the data of several experiments shown in Table 2. The symbols with the subscripts hearing 1 and 2 refer to the values before and after switching-in different driers and the "gooseneck".

Hence, air resistance does not affect the maximum pressure but determines the size and escape frequency of the bubbles.

"Sensitivity" of the Manometer. It is important to establish just what limiting rate in the change of pressure can be registered by a manograph. In the present case the limit is the amount of inertia of the toluene manometer; this may be judged by the rate of lowering of the fluid level for an instantaneous drop in the pressure, which amounted in our experiments to 6 to 10 cm. It was consequently to be expected that, when the pressure in the system changed with a rate approximating this amount, the manometer could not follow the change in pressure and give accurate readings.

In fact, when the formation of the bubbles occurs with such frequency the steepness of the rise of the manogram is equal or approximate to the steepness of the drop, the height of the maxima becomes indeterminate (see Figure 6, on the left). With further increases in the rate (on the right) the frequency of bubbles formation becomes approximately equal to the frequency of the natural oscillations of the fluid level in the manometer, and these oscillations but not the actual pressure in the system, were registered by the manogram (the manogram in Figure 6 was taken in 20 seconds; the object: water).

Thus the manogram itself, unlike visual observations, makes it possible to judge for which rates its data are reliable and to distinguish the "reliable" maxima.

Consequently, there is a limit to the rate of increase in pressure at which it is still possible to obtain correct readings. For a U-shaped manometer 4 mm in diameter and a toluene column 30 cm in length, the limiting rate at a temperature of 25° may be considered 5 cm per second.

The Effect of the Velocity of the Air Current. In the case of individual fluids, the maximum pressure does not depend on the velocity of the air current for smaller than limiting velocities. It is a different matter in the case of solutions of particularly surface-active substances and substances with a high viscosity.

The most characteristic result was produced by a ~ 0.1% soap solution. The left side of Figure 7 shows a manogram taken with a small opening of the micro-cock, the right side shows it with a full opening (duration of the whole exposure: 40 seconds). The maxima in the latter case were almost 1 cm greater than in the former.

From these statements it is evident that a manograph can be advantageously used for observation of the kinetics of formation of an adsorption layer down to the limit velocities determined by the data of the manometer.

The work was conducted under the direction of Professor N. A. Trifonov.

Conclusions

1. The investigation was conducted with the aid of a photorecording manometer ("manograph"), which registers the changes of pressure during the process of forming bubbles under different experimental conditions.

2. The size of a gas bubble breaking away from the capillary tip is not identical with its dimensions according to the Cantor-Schrodinger formula for maximum pressure and depends on the construction properties of the apparatus and the viscosity of the fluid.

3. The value of maximum pressure depends not on the resistance exerted against the air by the different parts of the apparatus, but exclusively on the constant of the capillary tip and the surface tension of the fluid.

4. There is a certain limiting rate of pressure change beyond which a toluene manometer, due to a certain inertia, cannot accurately register the true pressure in the system.

5. The suggested manographic method can be applied to measuring objectively and accurately and can be generally used in laboratory practice for observing the kinetics of pressure variation.

6. Measuring the drop in pressure after the escape of a gas bubble is recommended as a method for the approximate determination of viscosity.

Laboratory of Physical and Colloidal Chemistry,
Rostov State University imeni V. M. Molotov
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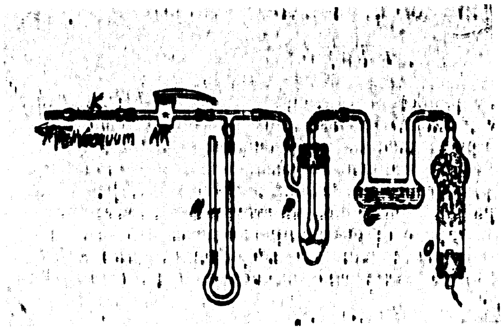

Figure 1. Rebinder's apparatus for measuring the surface tension of fluids; for explanation, see text.

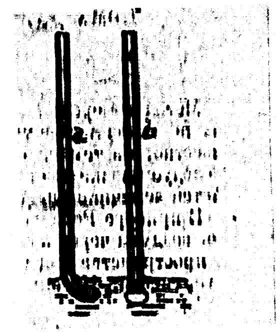

Figure 2. Illustration of a bubble breaking away from the capillary tip when the latter is in different positions.

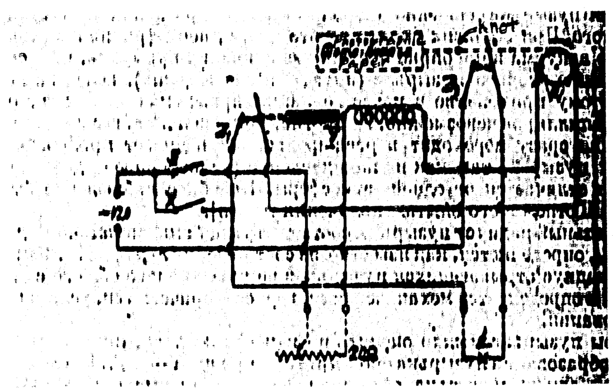

Figure 3. Diagram of the Electrical circuit of the apparatus for measuring the surface tension of fluids.

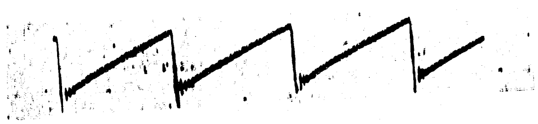

Figure 4. "Manogram" obtained by automatic recording.

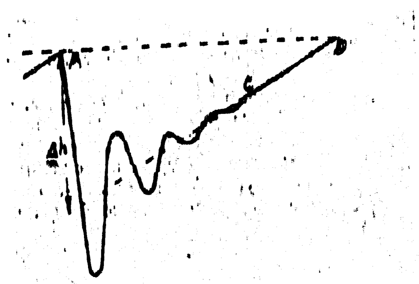

Figure 5. Graph of the pressure variation during the formation of a bubble.

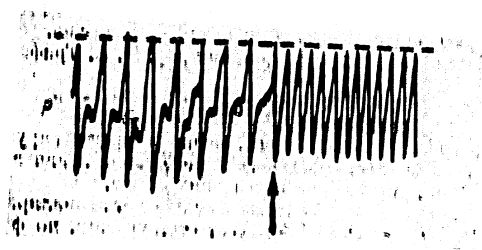

Figure 6. Effect of the inertia of the manometric fluid on the value of the maximum pressure for bubble formation

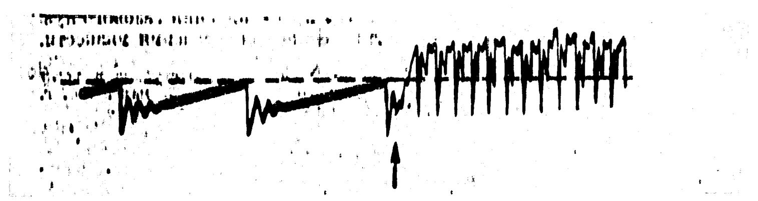

Figure 7. Effect of the velocity of the air current on the value of the maximum pressure for bubble formation

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